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Uncertainties in the oxygen isotopic composition of barium sulfate induced by coprecipitation of nitrate

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Coprecipitation of nitrate and sulfate by barium has probably resulted in significant error in numerous studies dealing with the oxygen isotopic composition of natural sulfates using chemical/thermal conversion of $BaSO_4$ and analysis by isotope ratio mass spectrometry. In solutions where NO_3^-/SO_4^{2-} molar ratios are above 2 the amount of nitrate coprecipitated with $BaSO_4$ reaches a maximum of approximately 7% and decreases roughly linearly as the molar ratio decreases. The fraction of coprecipitated nitrate appears to increase with decreasing pH and is also affected by the nature of the cations in the precipitating solution. The size of the oxygen isotope artifact in sulfate depends both on the amount of coprecipitated nitrate and the $\delta^{18}O$ and $\Delta^{17}O$ values of the nitrate, both of which can be highly variable. The oxygen isotopic composition of sulfate extracted from atmospheric aerosols or rain waters are probably severely biased because photochemical nitrate is usually also present and it is highly enriched in ^{18}O ($\delta^{18}O \sim 50$–90‰) and has a large mass-independent isotopic composition ($\Delta^{17}O \sim 20$–32‰). The sulfate $\delta^{18}O$ error can be 2–5‰ with $\Delta^{17}O$ artifacts reaching as high as 4.0‰. Copyright © 2008 John Wiley & Sons, Ltd.

Stable oxygen isotopes are important tools that can be used to trace the production, and removal, of atmospheric sulfate, arguably the most important compound in the global sulfur cycle and one that has a profound influence on global climate. Atmospheric sulfate (SO_4^{2-} found in aerosols and precipitation) plays an important role in climate because it is one of the most abundant compounds found in aerosols,[1,2] which in turn contribute to the direct (light scattering) and indirect (cloud formation) aerosol effect. It is also the main end product of the oxidation of reduced sulfur species and results in the formation of acid rain.[3,4] The pioneering work of Holt and Kumar,[5–9] along with others,[10] demonstrated that the $\delta^{18}O$ values in atmospheric sulfate can be used to trace the different pathways that oxidize reduced sulfur. These studies showed that the $\delta^{18}O$ value of atmospheric sulfate was largely controlled by the $\delta^{18}O$ of tropospheric water because S(IV) rapidly achieves isotopic equilibrium with liquid water. However, the subsequent oxidation pathways that convert S(IV) species into S(VI), referred to as 'secondary' sulfates, also influence the ultimate $\delta^{18}O$ value of atmospheric sulfate.[11] The main oxidation pathway for secondary sulfate is the gas-phase oxidation of SO_2 via the OH radical.[12] Aqueous phase heterogeneous oxidation of

dissolved SO_2 by O_2, H_2O_2 or O_3 is also an important source of SO_4^{2-} in clouds, fog and precipitation.[13,14] 'Primary' sulfate formed via high-temperature O_2 oxidation of SO_x in smoke stacks of coal-fired power plants is also thought to be regionally important.[6,8,15,16] Observations of atmospheric sulfate $\delta^{18}O$ values above those expected from only gas and aqueous oxidation processes have been attributed to the mixing of primary and secondary sulfates and isotopic disequilibrium.

Recently, there has been much interest in anomalous ^{17}O enrichments in sulfate that is produced photochemically and subsequently deposited to surfaces.[17–23] The standard notation for these anomalous enrichments is the capital delta notation:

$$\Delta^{17}O \sim \delta^{17}O - 0.52 * \delta^{18}O \qquad (1)$$

where δ^xO is the standard notation for the difference between the ratio of the minor (17,18) to major (16) oxygen isotope in a sample relative to the same ratios in standard mean ocean water (SMOW).[24] It has been suggested that the origin of positive $\Delta^{17}O$ values observed in atmospheric sulfate, and the seasonal trends, are a result of shifts in the relative importance of homogenous (gas phase) and heterogeneous (aqueous) SO_2 oxidation pathways.[19] Therefore, both the $\delta^{18}O$ and the $\Delta^{17}O$ values in atmospheric sulfate may provide clues as to which chemical pathways are important for atmospheric sulfate production.

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Since sulfate is isotopically preserved in soils and water, the unique oxygen isotope signature of atmospheric sulfate has been utilized as a proxy for detecting atmospheric deposition.[21–23] In a recent study on soils from the Atacama Desert in northern Chile, we observed large $\Delta^{17}O$ values (1–5‰) in soil sulfates.[25] In a subsequent study using sulfates obtained from Rech *et al.*,[26] it was found that some of the samples showed a much higher degree of $\delta^{18}O$ and $\Delta^{17}O$ deviation between replicate analyses (~5‰ for $\delta^{18}O$, 1–2‰ for $\Delta^{17}O$) than would be expected from the analytical uncertainty of 1‰ ($\delta^{18}O$) and 0.1‰ ($\Delta^{17}O$).[27] This only occurred when the extracts also had a significant amount of nitrate. Atacama soil nitrate has $\delta^{18}O$ and $\Delta^{17}O$ values of ~50‰ and ~19‰, respectively, which is attributed to the accumulation of atmospheric nitrate.[25] Since the precision of the sulfate oxygen isotope analysis deteriorated only in samples that also contained nitrate we initiated a series of control experiments to test the precision and accuracy of SO_4^{2-} isotopic analysis when samples are prepared by barium precipitation in the presence of nitrate. These test sulfates were then analyzed using three common isotope ratio mass spectrometry techniques: (1) the CO pyrolysis method, (2) the offline C reduction (and fluorination) method, and (3) the BrF_5 laser fluorination system. The objective of the experiments was to assess whether the presence of nitrate in a nitrate/sulfate solution had an impact on the $\delta^{18}O$ and $\Delta^{17}O$ values of the $BaSO_4$ precipitate.

EXPERIMENTAL

The experimental design was to obtain $BaSO_4$ from two sulfate solutions, one that was nitrate-free and the other that contained various amounts of an isotopically unique nitrate salt. A lab standard sulfate (Na_2SO_4; Fisher Scientific, Pittsburgh, PA. USA) was mixed to a concentration of 1.5 M and aliquoted in order to obtain ~100 µmol of SO_4^{2-} in 30 mL. A control set of $BaSO_4$ was prepared by heating the sulfate solutions to 80°C followed by precipitation using a slight excess of 1 M $BaCl_2$. Some samples were acidified after the heating step using a few drops of 1 M HCl. Heating and acidification are carried out on natural samples to eliminate possible interference by barium carbonate precipitation and to help form idealized $BaSO_4$ crystals.[27] Precipitations of $BaSO_4$ were also carried out in the presence of the nitrate isotope standard USGS35 ($NaNO_3$ form), the first $\Delta^{17}O$ standard, which has an established $\delta^{18}O$ value of 51‰ and a $\Delta^{17}O$ value of +21.6‰.[28,29] USGS35 was added in order to produce solutions with NO_3^-/SO_4^{2-} molar ratios ranging from 0.05 to 10, similar to those found in natural samples from aerosols, precipitation, and runoff. Each $BaSO_4$ precipitate was centrifuged, decanted and rinsed with Millipore water, three times. Ion chromatography analysis of the final rinse indicated that, at most, only a few nanomoles of NO_3^- remained in solution (e.g. ~0.001%) that could crystallize with the $BaSO_4$ upon drying. After being dried, several of the samples were ground and onceagain rinsed in Millipore water before the final drying.

In order to evaluate our data in the context of numerous prior studies on sulfate oxygen isotopes we chose to utilize three different isotope ratio mass spectrometry (IRMS) methods. The first method tested is currently the standard means for sulfate $\delta^{18}O$ analysis, thermal conversion elemental analysis (TC/EA).[30] The second method is the offline graphite reduction of $BaSO_4$ to CO_2 and CO followed by disproportionating the CO into C and CO_2 followed by analysis of the CO_2 using dual-inlet IRMS.[31,32] The third analytical approach uses laser fluorination to generate O_2 from $BaSO_4$ as described by Bao and Thiemens.[27]

The TC/EA method utilized a Costec Autoanalyzer (Valencia, CA. USA) interfaced to a Thermo Delta XP (ThermoFinnigan, Bremen, Germany) continuous flow IRMS instrument (also called CO-CFIRMS). $BaSO_4$ (~0.2–0.3 mg) is loaded into silver cups that are dropped into a high temperature (1425°C) carbon reduction chamber. The subsequent product CO is purified on a fused-silica Molesieve 5A chromatography column (Varian #CP7536; Palo Alto, CA. USA) and injected into the IRMS instrument using a Thermo Conflow open split. $\delta^{18}O$ determinations are made by calibration using isotopic reference materials such as NBS127 ($BaSO_4$), NIST 8549 (KNO_3), and NIST 8542 (Sucrose). Because of isobaric interface between ^{13}CO and $C^{17}O$, $\delta^{17}O$ determinations were not possible using CO-CFIRMS.

The offline carbon reduction method was carried out in vacuum using a device described by Sakai and Krouse.[33] A mixture of graphite and $BaSO_4$ is preheated to 400–500°C in a platinum foil boat connected to a resistance heater for 5 min to drive off water before raising the temperature to 1100°C. Evolved CO_2 is cryogenically separated using liquid nitrogen and residual CO is disproportionated to C and CO_2 using parallel platinum foil discharge plates and a current controlled by a Variac. The discharge product CO_2 is combined with the initial pyrolysis CO_2 giving yields that are typically >95% of sulfate on an oxygen basis. The CO_2 was analyzed using a dual-inlet Thermo DeltaXP IRMS instrument for $\delta^{18}O$ determination. We used the nitrate-free Fisher Scientific $BaSO_4$ as our internal standard for these samples. For $\Delta^{17}O$ determination, one sample of CO_2 was fluorinated with BrF_5 using standard protocols[34] resulting in an O_2/CF_4 mixture that was cryogenically purified and the O_2 was analyzed using a Finnigan-Mat 251 (ThermoFinnigan) dual-inlet IRMS instrument. This method was only tested using $BaSO_4$ precipitated from a 1:1 NO_3^-/SO_4^{2-} molar solution.

Details of the laser fluorination procedure can be found elsewhere.[27] Briefly, ~10 mg of $BaSO_4$ are weighed into a stainless steel sample target and loaded into the laser fluorination chamber that is then heated to 100°C and pumped to 10^{-6} Torr overnight. The following day the chamber is etched at room temperature with ~30 Torr of BrF_5 that will react with any absorbed water that is not eliminated during the pumping stage. The samples are lased[27] in the presence of 30 Torr BrF_5 and the resulting O_2 is then purified and analyzed using a Finnigan MAT 251 dual-inlet IRMS instrument.
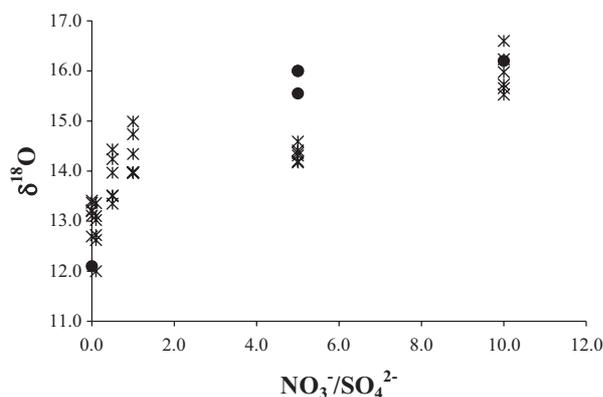
Figure 1. $\delta^{18}O$ values for CO and CO$_2$ derived from BaSO$_4$ precipitated out of solutions with various NO$_3^-$/SO$_4^{2-}$ molar ratios using USGS35 NO$_3^-$ ($\delta^{18}O = 57.5$‰)[27] and analyzed using (CO-CFIRMS) (stars) and the offline graphite reduction technique (solid circles).

RESULTS

The results of the oxygen isotopic analysis of the test sulfates are given in Figs. 1 and 2. For the CO-CFIRMS method the BaSO$_4$ derived from the pure SO$_4^{2-}$ solutions had $\delta^{18}O$ values of 13.1‰ relative to VSMOW with a precision of ±0.2‰, typical of continuous flow techniques. For BaSO$_4$ samples derived from solutions with NO$_3^-$/SO$_4^{2-}$ molar ratios of 0.5 and higher there is a clear positive $\delta^{18}O$ bias, reaching as high as 3.8‰ at the highest molar ratios. There are similar $\delta^{18}O$ biases in the CO$_2$ produced from BaSO$_4$ using the offline

graphite reduction whenever nitrate is present in the solution, with a maximum bias of 3.3‰ for 1:1 molar solutions. Similarly, the laser fluorination analysis of Fisher BaSO$_4$ shows no anomalous ^{17}O enrichment as expected for commercial grade sulfates that are produced by S oxidation using water ($\delta^{18}O$ approx. −10‰, $\Delta^{17}O$ ~0‰) and O$_2$ ($\delta^{18}O$ ~23‰, $\Delta^{17}O$ approx. −0.2‰).[35,36] In contrast, every sulfate precipitated in the presence of USGS35 has significantly higher $\Delta^{17}O$ values ranging from 0.1‰ to 1.7‰. The single CO$_2$ sample prepared using the offline technique and fluorinated using BrF$_5$ had a $\Delta^{17}O$ value of 0.3‰, similar to those in 1:1 solutions analyzed using the laser fluorination method. Spurious $\Delta^{17}O$ values can result from fluorination of NO$_2$ that may have been produced during the C pyrolysis or fluorination of nitrate. This can produce NF$_3$ leading to a false signal at m/z 33 from the NF$^+$ fragment ion generated in the ion source.[37] However, we observed no ion at m/z 52 (NF$_2^+$) and purification of the produced O$_2$ by molecular sieve[38] and gas chromatography did not alter the $\delta^{18}O$ or $\Delta^{17}O$ values. In addition the NF$^+$ ion would not have a large influence on $\delta^{18}O$ differences, and no NF$^+$ would be present in the pyrolysis techniques since no fluorine is used in those methods. We therefore ruled this out as the source of any isotopic bias.

The isotopic bias appears to be a function of the chemical properties of the solutions (Fig. 1). There is a correlation between the $\delta^{18}O/\Delta^{17}O$ bias at low NO$_3^-$/SO$_4^{2-}$ ratios but this plateaus at ratios above 1. The asymptote observed in the $\Delta^{17}O$ data (Fig. 2) is less clear in the $\delta^{18}O$ data mainly due to the 5:1 molar ratio data grouping, whose $\delta^{18}O$ value is about 1.5‰ lower relative to the trend expected from the $\Delta^{17}O$ data. When the NO$_3^-$/SO$_4^{2-}$ molar ratios are below 2, BaSO$_4$ originating from the warm, acidified solutions (pH ~2–3) appear more positively biased relative to the neutral solutions, but this pH effect diminishes at higher molar ratios. This is not due to water–sulfate isotopic exchange because the pH is sufficiently high and precipitation removes SO$_4^{2-}$ rapidly (minutes) and these together would limit significant exchange.[39] In addition, the observed isotope effect goes in the opposite direction, i.e. positive $\delta^{18}O$ and $\Delta^{17}O$ biases, where water would induce a decrease in the $\delta^{18}O$ value because of the negative $\delta^{18}O$ of the local water (approx. −10‰) and zero $\Delta^{17}O$ values. Precipitates prepared on different days with the same molar ratios had good $\Delta^{17}O$ precision (±0.2‰), but, in solutions whose total molarity differed by a factor of 3 (e.g. more concentrated solutions), we observed false $\Delta^{17}O$ values of 1.1‰ vs. 0.4‰ for the more dilute solutions (Fig. 2).

Figure 2. Artifact sulfate $\Delta^{17}O$ values of BaSO$_4$ precipitated from solutions with various NO$_3^-$/SO$_4^{2-}$ molar ratios of USGS35 nitrate ($\Delta^{17}O = 21.6$‰) and Fisher brand Na$_2$SO$_4$ (■, $\Delta^{17}O = -0.1$‰) for neutral and acidic solutions. Fit line A is from the experimental data and fit line B is the possible artifact assuming a nitrate $\Delta^{17}O = 31$‰, typical of Antarctica soils and the high end of nitrate aerosol $\Delta^{17}O$ values. The X markers on the right-hand side are the published $\Delta^{17}O$ values for sulfates from aerosols, rainwater, dusts, soils and minerals as described in the text.

DISCUSSION

The results indicate that a significant amount of NO$_3^-$ is coprecipitating with the barite leading to spurious sulfate $\delta^{18}O$ and $\Delta^{17}O$ values. The sulfate $\delta^{18}O$ values, as determined by the TC/EA method, show a clear increase for BaSO$_4$ that was precipitated in the presence of USGS35. The degree of contamination can be established from the mass balance equation:

$$\delta^{18}O\,CO = s \times \delta^{18}O\,SO_4^{2-} + n \times \delta^{18}O\,NO_3^- + \varepsilon \qquad (2)$$

where the CO is generated by CO-CFIRMS, s and n correspond to the fractions of CO derived from the sulfate and nitrate anions during reduction, and ε is the enrichment factor associated with any fractionation of oxygen isotopes by the reduction if there is less than a 100% yield (negligible for the current case where yields are >90‰). Taking the pure $BaSO_4$ $\delta^{18}O$ value (13.1‰) and USGS35 nitrate $\delta^{18}O$ as 51‰, then, using Eqn. (2), the maximum $\delta^{18}O$ shift of ~3.5‰ corresponds to a contamination of about 6.8% from USGS35 nitrate. Figure 1 suggests that the fraction of oxygen originating from NO_3^- decreases as the NO_3^-/SO_4^{2-} molar ratio decreases and that it is indiscernible at ratios of less than 0.1.

A similar mass balance equation to Eqn. (2) can be derived using $\Delta^{17}O$ by replacing $\delta^{18}O$ with $\Delta^{17}O$ and CO with O_2. The $\Delta^{17}O$ value of the initial Na_2SO_4 is –0.1 (relative to our VSMOW normalized O_2 standard) and, for USGS35 NO_3^-, the $\Delta^{17}O$ value is 21.6‰. Using the $\Delta^{17}O$ version of Eqn. (2), estimates of nitrate contamination ranged from 1.2% to 8.0% in neutral solutions and from 6.2 to 7.7% for acidified solutions, which are similar to those obtained using the $\delta^{18}O$ mass balance. Again there is a weak correlation between the degree of NO_3^- contamination and lower molar ratios, but it is not strictly linear and even the NO_3^-/SO_4^{2-} solutions with 0.1 and 0.05 molar ratios have significant $\Delta^{17}O$ artifacts.

The resulting sulfate isotopic artifact (error) can be estimated by:

$$\delta^{18}O \text{ artifact} = x * y * \delta^{18}O\, NO_3^- + \varepsilon \qquad (3)$$

where x is the mole fraction of nitrate coprecipitated, y is the mole fraction that nitrate converted into $CO/CO_2/O_2$ relative to sulfate conversion (method dependent), ε is an enrichment factor related to the incomplete conversion of NO_3^- to the gas to be analyzed, and $\delta^{18}O\, NO_3^-$ is the $\delta^{18}O$ value of the nitrate. A similar equation in $\Delta^{17}O$ can be formulated but, in this case, ε is zero as no known non-photochemical process can generate a non-zero $\Delta^{17}O$ value. The good precision at a given molarity suggests that the relative amount of oxygen derived from NO_3^- and SO_4^{2-} is always consistent (y in Eqn. (3)) but the amount of nitrate coprecipitation may be variable (x in Eqn. (3)) depending on solution conditions such as pH, cation species and concentration.

The high solubility of all nitrate salts would suggest that $Ba(NO_3)_2$ precipitation does not occur and that this is an inclusion or absorption phenomenon. Our review of the literature revealed that nitrate coprecipitation with sulfate was the subject of several papers in the 1930s. Schneider and Rieman found that between 5 and 20% of the $BaSO_4$ crystal was occluded nitrate when precipitated from 1:1 NO_3^-/SO_4^{2-} solutions at 0.10 M concentrations and neutral pH.[40] An excess of barium tended to occlude more nitrate than when barium was below stoichiometric equivalence. X-ray diffraction studies indicated that nitrate was substituting for sulfate in the crystal lattice rather being occluded, which prohibited nitrate removal by additional washings.[41] An interesting observation in this study was that the amount of nitrate coprecipitated (~4% wt.) was virtually independent of the nitrate concentration, in general agreement with our results which show a plateau of the $\delta^{18}O$ and $\Delta^{17}O$ artifacts for a 10-

fold differences in nitrate concentration (Figs. 1 and 2). Nichols and Smith found that in basic solutions only 2% of the weight of $BaSO_4$ was nitrate and that it was an absorption phenomenon rather than occlusion or crystal substitution.[42] Although there was debate concerning the mechanism (occlusion, absorption or lattice substitution), each study conclusively showed that coprecipitation of nitrate with $BaSO_4$ does occur at molar ratios of 0.10 or less and that washing the $BaSO_4$ did not eliminate the nitrate contamination. Later work showed that the cation species is also important, with nitrate coprecipitation being greatest in the presence of K^+ and decreasing in order with NH_4^+, Na^+ and Li^+.[43]

The $\delta^{18}O$ and $\Delta^{17}O$ results presented here support these coprecipitation conclusions. Our percentages of coprecipitated nitrate, based on $\delta^{18}O$ and $\Delta^{17}O$ values, are in the same range as those found analytically and we also find that low pH enhances the coprecipitation at low molar ratios. The precise amount of nitrate coprecipitated based on $\delta^{18}O$ or $\Delta^{17}O$ is difficult to determine because it is less clear how much of the coprecipitated nitrate is actually being converted into CO and O_2 during analysis. Oxygen yields for sulfate in the laser fluorination method are only ~30% and lasing pure $Ba(NO_3)_2$ as a yield experiment would probably give different results from those from the actual lasing the mixed crystal. Yields for the CO_2 fluorination are greater than 90%, but the amount of nitrate converted into CO_2 during the pyrolysis portion of the method is also ambiguous because some nitrate may decompose to NO_2 which would be cryogenically retained at $-80°C$ in the water-removal trap. Nitrate salts have been quantitatively converted into CO_2 by graphite pyrolysis but this usually occurs in closed vessels, which are allowed to equilibrate, and conversion yields depend on the cation of the salt and the reduction conditions.[44] However, the similarity between the $\Delta^{17}O$ artifact in the laser fluorination technique and the C reduction-CO_2 fluorination technique (~0.3‰) suggests that the yield of nitrate oxygen is similar for both methods.

The $\delta^{18}O$ bias that we observe in nitrate-contaminated $BaSO_4$ using the TC/EA-IRMS system and offline C reduction raises questions as to the accuracy of numerous sulfate $\delta^{18}O$ studies involving aerosol, rainwater, stream and soil sulfates that have the potential to be influenced by nitrate contamination. Nitrate is normally present in the atmosphere as particulate matter or gaseous HNO_3, both of which are incorporated into precipitation and bulk aerosols. Nitrate is often the dominant anion in urban areas that are far removed from oceanic and coal combustion sulfate sources. Even in sulfate-dominated regions, such as the upper Midwest region of the United States, the NO_3^-/SO_4^{2-} ratios in precipitation are still ~1 (see NADP database[45]). Nitrate produced in the atmosphere at mid-latitudes has average $\delta^{18}O$ values of approximately 70‰ but which can be as high as 90‰,[46–48] and this would produce sulfate $\delta^{18}O$ errors of 4–6‰ based on the nitrate coprecipitation amounts of ~6.5%. This is significant given that the range of published atmospheric sulfate $\delta^{18}O$ data typically varies in the order of 5–10‰.[8,10,49] It is likely that this has led to the misinterpretation of seasonal variations in the $\delta^{18}O$ values of atmospheric sulfate. It is difficult to establish which

studies may have biases because many of these studies did not report NO_3^- concentrations and there are subtle differences in methodology such as the pre-heating temperature/time and concentration/cleanup methods that are too numerous for us to test in a reproducible manner. For example, in a method still used today, Cortecci and Longinelli[50] pre-concentrated dilute sulfate solutions on the anion exchanger hydrous zirconium oxide that is 'purified' using nitric acid. When the pH is raised to desorb the sulfate, nitrate is also likely to desorb but was probably not detected because the control sulfate $\delta^{18}O$ value of 10‰ is similar to the $\delta^{18}O$ values of commercial nitric acids and nitrates (10–18‰).

The nitrate contamination can also produce $\Delta^{17}O$ values that are equal to those found in sulfate minerals and aerosols.[19–23,51–53] Atmospheric nitrate from mid-latitudes has $\Delta^{17}O$ values from 20–30‰,[46] which could generate $\Delta^{17}O$ biases as high as 3‰, based on the percentage of coprecipitation that we observe. Aerosol and rainwater sulfate $\Delta^{17}O$ values were previously attributed to SO_x oxidation by ozone in the aqueous phase, but there could be a $\Delta^{17}O$ bias if nitrate, another common aerosol anion, is present in the precipitation solution. Similar biases may be present in mineral sulfates that were extracted from soils that contain significant amounts of nitrate such as those from the Atacama Desert[54] and the McMurdo Dry Valleys of Antarctica.[55] Bao et al. recently reported $\Delta^{17}O$ values of 1–5‰ for Antarctic Dry Valley soil sulfate[22] that coexist with % levels of nitrate, which have $\Delta^{17}O$ values of ~30‰.[56] A reanalysis of these samples revealed a $\Delta^{17}O$ bias in excess of 4‰ for NO_3^-/SO_4^{2-} molar ratios as low as 0.28.[57] Due to the variable amounts of nitrate coprecipitated depending on solution conditions (pH, cation content, temperature) it is unlikely that the artifacts can be corrected based on nitrate concentration data alone. A method for eliminating nitrate contamination has recently been published[57] that should be adopted as part of the preparation procedure of BaSO$_4$ for solutions containing nitrate and sulfate. Nitrate contamination would not affect studies[17,18] that used analytical methods that avoid the BaSO$_4$ precipitation step, such as the thermal decomposition of Ag_2SO_4,[58] and thus would not have the isotopic bias.

CONCLUSIONS

We have shown that the standard preparation of sulfate samples for oxygen isotopic analysis by precipitation with barium can be significantly influenced by coprecipitation of the nitrate anion. Three different isotopic techniques show that up to 7% of the oxygen derived from BaSO$_4$ can actually be originating from coprecipitated NO_3^-. The degree of contamination depends on the precipitation conditions including NO_3^-/SO_4^{2-} molar ratios, pH, solution cations and overall solution concentrations. The magnitude of the isotope error depends not only on the degree of contamination, but also on the $\delta^{18}O$ and $\Delta^{17}O$ values of the nitrate in solution, which can be highly variable. It is likely that many studies examining $\delta^{18}O$ and/or $\Delta^{17}O$ values and trends in atmospheric sulfates (aerosols, precipitation, snow) that used the BaSO$_4$ methodology are positively biased because of the failure to eliminate NO_3^- during sample preparation. This is because NO_3^-/SO_4^{2-} molar ratios are significant (~0.5–10) in atmospheric samples and because atmospheric NO_3^- has uncharacteristically high $\delta^{18}O$ and $\Delta^{17}O$ values. Terrestrial samples are likely to be less severely influenced by the contamination because NO_3^- is typically only available in trace amounts and has low $\delta^{18}O$ and $\Delta^{17}O$ values. However, in systems where terrestrial sulfate and nitrate are highly influenced by the atmosphere, and BaSO$_4$ is the isotopic analyte, the positive bias is likely to be significant.

Possible solutions to the coprecipitation problem are: barite digestion, heating BaSO$_4$ above the Ba(NO$_3$)$_2$ decomposition temperature, or removal of the nitrate prior to precipitation by chemical reduction, precipitation (Nitron) or bacterial reduction. Bao[57] has recently reported that the contamination can be eliminated by repeated precipitation and dissolution using a chelating agent. Alternatively, one can avoid BaSO$_4$ precipitation and use the chromatographic separations and thermal decomposition of Ag_2SO_4 as described by Savarino et al.[58] Any of these nitrate-removal processes should be carefully tested for isotope effects and a sulfate $\Delta^{17}O$ and $\Delta^{33}S$ standard, similar to USGS35, should be developed to better control the accuracy of oxygen and sulfur isotope analytical techniques. New, more accurate analysis of $\delta^{18}O$ and $\Delta^{17}O$ variations in atmospheric sulfate using improved analytical techniques may yield more interesting seasonal and special variability that was previously masked by nitrate-induced artifacts.

Acknowledgements

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